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SIGNIFICANT LIQUID STRUCTURES, VI. THE VACANCY THEORY OF LIQUIDS

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The liquid state is stable in a temperature range intermediate between that of solid and vapor. Usually, the liquid density is also intermediate. Exceptional substances such as water involve a structural shrinkage superposed on the usual expansion of the solid to liquid transition. It is natural to seek an explanation of the intermediate liquid state as an intimate mixture of solid and vapor. All the imperfections of the solid state should be even more abundant in the liquid. However, those imperfections which yield a large ratio of entropy increment to enthalpy increment will be correspondingly more abundant in the liquid and will be the significant structures in a quantitative theory.

The Liquid Model.—Holes of molecular size are assumed overwhelmingly abundant because (a) they confer gas-like properties on a neighboring molecule jumping into the hole and (b) a solid-like molecule obtains a positional degeneracy equal to the number of neighboring vacancies. Neglecting increase in volume due to holes of other than molecular size, the number of holes per mole of molecules is $(V - V_s)/V_s$, where V and V_s are the molal volumes of liquid and solid, respectively. The chance that a vacancy confers gas-like properties on a neighboring molecule is assumed proportional to the fraction of neighboring positions populated by molecules. This fraction is V_s/V if molecules and vacancies are randomly distributed. Thus, for random distribution of vacancies, the mole fraction of gas-like molecules is $(V_s/V)(V - V_s)/V_s \equiv (V - V_s)/V$. The remaining mole

fraction, V_s/V , of molecules are solid-like. The specific heat at constant volume for a liquid such as argon should thus be well represented by the equation

$$C_v = \frac{V_s}{V} 6 + \frac{(V - V_s)}{V} 3. \quad (1)$$

This is seen to be the case in Figure 1. This estimate of the number of solid-like and gas-like molecules was initiated by Walter and Eyring¹ in 1941.

The average number of vacancies next to a molecule if vacancies are randomly distributed is then

$$\frac{Z(V - V_s)}{V} = \left(\frac{ZV_s}{V} \right) \frac{V - V_s}{V_s} \equiv \frac{n(V - V_s)}{V_s}. \quad (2)$$

Here Z is the number of nearest neighbors and $(V - V_s)/V$ is the fraction of the neighboring positions occupied by vacancies. Since most simple liquids approximate a close-packed structure at the melting point, Z should have the value 12 and V_s/V is about 0.9 so that one expects $n \simeq 10.8$, which is the value which best fits the thermodynamic data for argon. It is natural to suppose that of the possible positions available to a molecule some one is energetically favored over the others by the way the neighbors are organized about it. This difference in energy between the best position and the average for the neighboring available positions should be proportional to the energy of sublimation, E_s , and inversely proportional to n_h , the number of holes; i.e. it should have the value $aE_s/n_h = aE_sV_s/(V - V_s)$. Figure 2 illustrates the energetic situation for a solid-like molecule comparing the most favored position with a neighboring vacancy.

It is now possible to write down the partition function, f , for a mole of rare gas such as argon

$$f = \left\{ \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \left(1 + n \frac{V - V_s}{V_s} e^{-\frac{aE_sV_s}{(V - V_s)RT}} \right) \right\}^{\frac{NV_s}{V}} \times \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} (V - V_s) \right\}^{\frac{N(V - V_s)}{V}} \left\{ \left(\frac{N(V - V_s)}{V} \right)! \right\}^{-1}. \quad (3)$$

Using Stirling's approximation $X! = (X/e)^X$, this becomes

$$f = \left\{ \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \left(1 + n \frac{V - V_s}{V_s} e^{-\frac{aE_sV_s}{(V - V_s)RT}} \right) \right\}^{\frac{NV_s}{V}} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \right\}^{\frac{N(V - V_s)}{V}}. \quad (4)$$

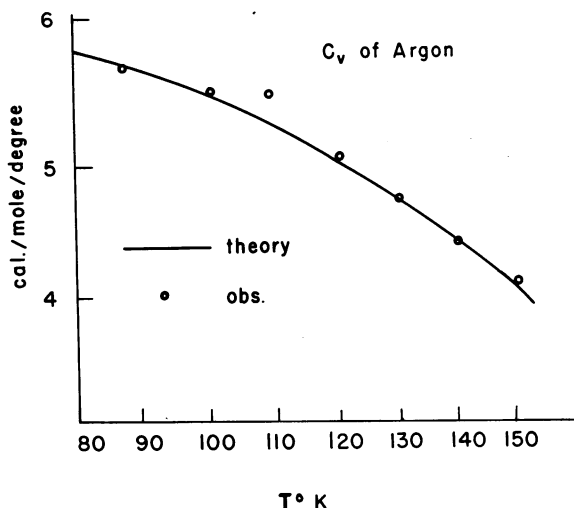


FIG. 1.—Specific heat of argon at constant volume plotted as a function of temperature. Circles represent observed values. The curve is a plot of equation (1).

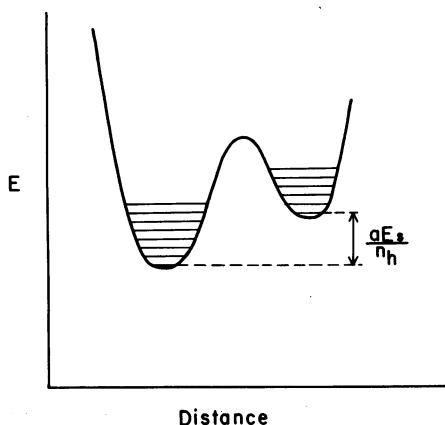


FIG. 2.—Potential curve for a molecule occupying the most favored position as compared with a neighboring vacancy.

Here N , θ , T , m , k , and h are Avogadro's number, the Einstein characteristic temperature of the solid, absolute temperature, mass of the molecule, Boltzmann's constant, and Planck's constant, respectively. The other quantities have been defined and the form of the partition function is determined by the model. The only constant not fixed by the model is a . The value of a required to fit the data is in accord with expectations that the energy for a molecule to move to a neighboring vacancy be small compared with the energy of sublimation, E_s .

In Table 1, the values obtained by Fuller, Ree, and Eyring² for the properties of argon using equation (4) are found.

In this table, V , ΔS , P , and T represent molal volume in cc, the entropy of phase change, pressure in atmospheres, and temperature in degrees Kelvin. The subscripts m , b , and c indicate the melting point, boiling point, and critical point, respectively; $\Delta(\%)$ is the percentage deviation of the calculated from the observed values.

TABLE 1

PROPERTIES OF ARGON

	V_m , cc	ΔS_m , eu	P_m , atm	V_b , cc	ΔS_b , eu	T_b , °K	T_c , °K	V_c , cc	P_c , atm
Calc	28.90	3.263	0.732	29.33	19.04	87.29	149.7	83.68	52.93
Obs	28.03	3.35	0.674	28.69	17.85	87.29	150.66	75.26	48.00
$\Delta(\%)$	+3.11	-2.61	+8.55	+2.22	+6.68	0	-0.637	+11.2	+10.3

$n = 10.80$ $a = 0.00534$ $E_s = 1888.6$ cal/mol
 $V_s = 24.98$ cc $\theta = 60.0^\circ\text{K}$

It should be stressed that our theory does not regard the liquid state as a mixture of solid and gas. A molecule has solid-like properties for the short time it vibrates about an equilibrium position, then it instantly transforms to gas-like behavior as it jumps into the neighboring vacancy. It is well known that nucleation of bubbles in boiling and crystal nucleation in freezing, if uncatalyzed, are very slow processes. These facts show that no solid or gaseous molecular arrangement as large as these nuclei exists in the liquid state.

Theory of Molten Salts.—The observed percentage change in volume of argon upon melting is 12 per cent. It is interesting to compare the theoretically expected volume change accompanying the melting of salts with the observed values as listed in Table 2.

Evidently the expansion of molten salts upon melting is about twice that of argon. (This is to be expected from our theory. The entropy of melting comes from the

TABLE 2

VOLUME CHANGES AT THE MELTING POINTS

	NaCl	KCl	NaBr	KBr
Liquid volume (cc)	37.74	48.80	44.08	56.03
Solid volume (cc)	30.19	41.57	36.02	48.05
Per cent change	25.0	17.4	22.4	16.6

randomness introduced by vacancies. Since positive ions can occupy only half the vacancies while negative ions can occupy the other half, it should require twice the percentage expansion to get the same entropy increase for each kind of ion. This is in accord with the observations. The fact that only half the extra volume ($V - V_s$) provides vacancies for each kind of ion means that n in the degeneracy term, $n(V - V_s)/V_s$, should be only about half as large for salts as for argon. This too is in accord with the findings, as one sees below.

The energy of vaporization for liquid argon (see equation (4)) falls off as $(E_s V_s)/V$, that is, inversely as the volume, as van der Waals suggested for gases long ago. This is not true for the molten salts since in one of the three dimensions, a Na^+ and Cl^- cling together and there is expansion only in the other two dimensions. Thus the energy should fall off more nearly inversely proportional to $V^{1/2}$.

Such considerations provide the justification for the following partition function used by Carlson, Eyring, and Ree³ for molten salts.

$$f = \left\{ \frac{\exp E_s/2RT(V/V_s)^{1/2}}{(1 - e^{-\theta/T})^3} \left(1 + n \frac{V - V_s}{V_s} e^{-\frac{aE_s V_s (V/V_s)^{1/2}}{(V - V_s)RT}} \right) \right\}^{\frac{2NV_s}{V}} \times \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \frac{8\pi^2 IkT}{h^2} \frac{1}{1 - e^{-h\nu/kT}} \right\}^{\frac{N(V - V_s)}{V}} \quad (5)$$

The results found by Carlson *et al.*³ for KCl are shown in Table 3. The properties in the gas-like part of the partition function are for the molecule of KCl.

TABLE 3
PROPERTIES OF FUSED KCl

	T_m , °K	V_m , cc	ΔS_m , eu	T_b , °K	V_b , cc	ΔS_b , eu	T_c , °K	V_c , cc	P_c , atm
Calc	1023	49.06	5.40	1684	71.20	21.63	3092	432	135.5
Obs	1049	48.80	5.8	1680	—	23.1	—	—	—
Δ (%)	-2.6	+0.53	-6.90	+0.24	—	-6.36	—	—	—
	$n = 6$		$a = 0.03000$		$E_s = 54.15$ kcal/mol				
	$V_s = 41.57$ cc		$\theta = 170^\circ \text{K}$		$I = 2.195 \cdot 10^{-48}$ gm cm ²				
	$\omega = 305$ cm ⁻¹								

Our vacancy liquid theory applies with equal faithfulness to molten metals if we recognize that the necessary vacancies need only be large enough to accommodate the ion stripped of the valence electrons and these ions are only about a third the volume of the atom. That the viscosity data indicate that the ions in liquid metals maneuver as though they were independent of their valence electrons was pointed out long ago.⁴ Thus, metals expand upon melting roughly one third as much as argon. Taking this into account by choosing values of n about three times as large as for argon and allowing for both atoms and diatomic molecules in the gas-like part of the partition function, the same faithful representation of thermodynamic and transport properties for the metals is obtained.⁵ Again, our model seems to be powerfully supported.

Surface Tension.—The partition functions for liquids used in this and earlier papers of the series reduce to the solid partition function when $V_s = V$ and to the gaseous partition function for $V \gg V_s$. It is therefore to be expected that such a partition function will represent the surface layer if proper account is taken of the density gradient. For a simple closepacked liquid such as argon, it is supposed that layers will orient so that a molecule tends to have six nearest neighbors in the

same layer, three neighbors below and three above. Only E_s , the bulk energy of sublimation, should be appreciably different for a surface and a bulk molecule. The energy E_{s_i} of a molecule in the i th surface layer is then given by the equation

$$E_{s_i} = E_s \left(\frac{6}{12} \frac{\rho_i}{\rho_i} + \frac{3}{12} \frac{\rho_{i+1}}{\rho_i} + \frac{3}{12} \frac{\rho_{i-1}}{\rho_i} \right). \quad (6)$$

Here ρ_i is the density of the i th layer and the subscript increases with depth in the liquid. When i is the top liquid layer and $i - 1$ the first gas layer, one can write

$$\rho_{i-1}/\rho_i = \exp \left\{ -\frac{E_s}{2RT} \left(1 - \frac{T}{T_c} \right) \right\}. \quad (7)$$

This corresponds to a molecule in the top liquid layer possessing 6 nearest neighbors in the same plane, 3 in the neighboring liquid plane, but none in the gas layer at low temperatures. A molecule in the first gas layer, on the other hand, has only the three neighbors in the first liquid layer with none in the same gas layer nor in the gas layer above. Thus, the extra binding energy of a molecule in the first liquid layer over one in the first gas layer corresponds to six more neighbors out of a possible twelve or an extra binding energy of $E_s/2$. In keeping with this result, the exponent of equation (7) reduces to $E_s/(2RT)$ at low temperatures and vanishes at $T = T_c$, as it must since the densities become equal at the critical temperature.

One now proceeds to calculate the Gibbs free energy per mole, $G_i = A_i + pV_i$, by an iterative process until self-consistency is achieved. For the surface layer, one can first guess the density ρ_i and then set ρ_{i+1} provisionally equal to the density of bulk liquid.

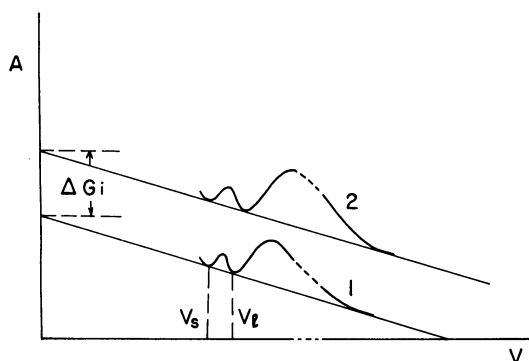


FIG. 3.—Schematic diagram of the Helmholtz free energy, A , plotted against volume at a fixed temperature for a bulk liquid (curve 1) and for a surface layer (curve 2). ΔG_i is the extra Gibbs free energy per mole of surface as compared with the bulk liquid.

Now after plotting A_i against V (cf. Fig. 3), the molal volume V_i of surface liquid can be obtained from the curve and is compared to V_i corresponding to the assumed value ρ_i . When, after repeated attempts, assumed and calculated values of V_i agree, one can recalculate ΔG_i for the layer i , etc. The whole procedure must continue until all assumed and calculated values of the density are self-consistent. The surface tension, γ , is then

$$\gamma = \sum_i \Delta G_i \frac{0.9165}{V_i} \left(\frac{V_s}{N} \right)^{1/3}. \quad (8)$$

The quantity $0.9165 (V_s/N)^{1/3}$ is the volume of a layer of solid lattice one square centimeter in area.

In Table 4, observed and calculated values of the surface tension of argon are given following Chang, Eyring, Ree, and Matzner.⁶

In Table 4, the columns give the temperature Kelvin, molal volume of the top liquid layer, molal volume of the vapor, percentage of the surface tension calculated

TABLE 4
 SURFACE TENSION OF ARGON (DYNE/CM)

$T^{\circ}\text{K}$	V_l , cc	V_g , cc	1st, %	2nd, %	3rd, %	Calc	Obs	Δ , %
83.85	28.90	10,208	87.16	12.84	0	13.78	13.5	+2.09
85.5	29.08	8,493	86.45	13.55	0	13.43	13.1	+2.52
87.29	29.33	6,944	85.87	14.13	0	13.02	12.6	+3.33
90.0	29.80	5,246	85.35	14.65	0	12.22	11.9	+2.69

for the first, second, and third liquid layers, the calculated surface tension, the observed surface tension, and the percentage discrepancy. This is another striking success for the vacancy liquid theory. Values for other liquids are to be found in the paper of Chang *et al.*⁶

The calculated densities of successive layers in the neighborhood of the surface were calculated for argon and are plotted in Figure 4.

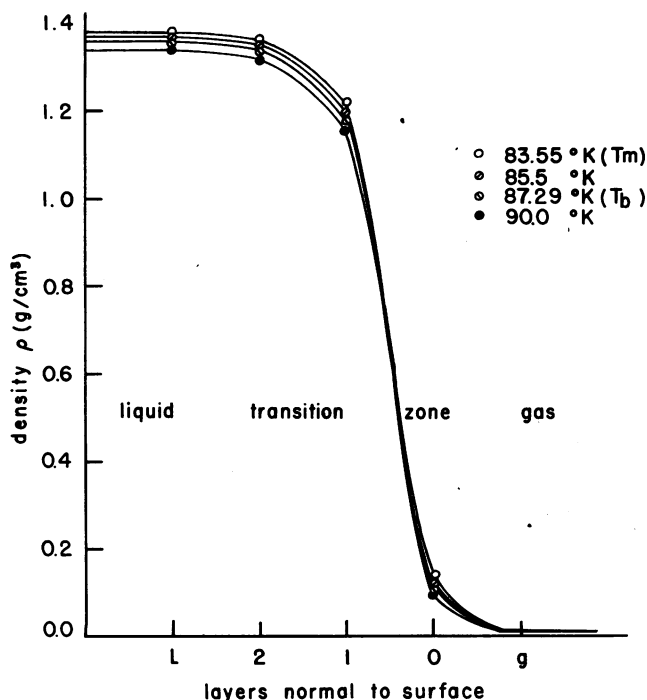


FIG. 4.—The density change in going from the liquid phase through the transition layers in the gas phase for argon at four temperatures.

Viscosity.—The vacancy theory of liquids has implicit in it a general theory of transport properties. Since there are solid-like and gas-like degrees of freedom in the liquid, both must be taken into account in calculating the viscosity. We follow the procedure outlined in the paper by Fuller, Ree, and Eyring (to be published). The shear plane lies between two molecular layers. If a fraction, x_s , of the shear plane is covered by solid-like molecules and the remaining fraction, x_g , by gas-like molecules, then the viscosity, η , which is the ratio of shear stress, f , to rate of strain, $\dot{\gamma}$, is

$$\eta = \frac{f}{\dot{s}} = \frac{x_s f_s + x_g f_g}{\dot{s}} = x_s \eta_s + x_g \eta_g = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g. \quad (9)$$

In accord with earlier procedure,⁷ we now calculate the viscosity of solid-like molecules, η_s . We can write

$$\eta_s = \frac{f}{\dot{s}} = f / \left\{ \sum_i \frac{\lambda \cos \theta_i k_i}{\lambda_1} \exp \frac{f \lambda_2 \lambda_3 \lambda \cos \theta_i}{2kT} \right\} \\ \simeq f / \left\{ \frac{\lambda}{\lambda_1} \sum_i k_i \left(\cos \theta_i + \frac{f \lambda_2 \lambda_3 \lambda \cos^2 \theta_i}{2kT} \right) \right\} \quad (10)$$

In Equation (10), \dot{s} is the rate of shear corresponding to the velocity with which one molecular layer slips over the other divided by λ_1 , the distance between layers

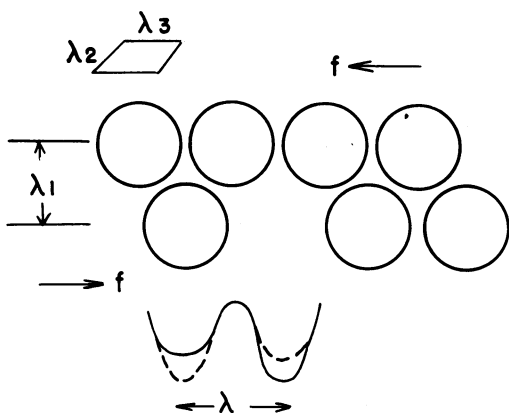


FIG. 5.—Distances between molecules in a liquid. λ is the distance between two successive equilibrium positions for viscous flow.

(cf. Fig. 5). k_i is the frequency of jumping into the i th neighboring empty lattice site for $f = 0$. When f is not zero, the work helping the molecule move forward is the force $f \lambda_2 \lambda_3$ multiplied by the component of the distance to the top of the barrier ($\lambda \cos \theta_i$)/2. Thus the rate of jumping into the i th site is $k_i \exp (f \lambda_2 \lambda_3 \lambda \cos \theta_i / 2kT)$ and the corresponding distance jumped is $\lambda \cos \theta_i$, so that $\sum_i \lambda \cos \theta_i k_i \exp (f \lambda_2 \lambda_3 \lambda \cos \theta_i / 2kT)$ is the velocity of the molecule due to all jumps into neighboring empty sites. Expanding the exponential gives the last form in equation (10). Since the sites are

randomly distributed over the solid angle, the first term in the summation of equation (10) has the value $\sum_i k_i \cos \theta_i = 0$ and the second term

$$\sum_i k_i \frac{f \lambda_2 \lambda_3 \lambda}{2kT} \cos^2 \theta_i = \left(\sum_i k_i \right) \frac{f \lambda_2 \lambda_3 \lambda}{6kT}. \quad (11)$$

Here we have used the fact that the average of $\cos^2 \theta$ over space is $1/3$.

According to our vacancy liquid theory, a solid molecule can jump into all neighboring empty sites, so that

$$\left(\sum_i k_i \right) = \kappa \frac{kT}{h} \frac{n(V - V_s)}{V_s} (1 - e^{-\theta/T}) \exp - \frac{a' E_s V_s}{(V - V_s) RT}. \quad (12)$$

In equation (12), we have supposed the activation energy is $a' E_s V_s / (V - V_s)$ in accordance with Figure 2 and that the partition function for normal and activated states cancel out in the rate expression except for the reaction coordinate where the partition function for the normal state introduces the factor $(1 - e^{-\theta/T})$. Using Equations (11) and (12) to simplify (10) gives:

$$\eta_s = \frac{\lambda_1 h \exp \{a' E_s V_s / (V - V_s) RT\}}{(\lambda^2 \lambda_2 \lambda_3 / 6) \kappa (1 - e^{-\theta/T}) n (V - V_s) / V_s} \quad (13)$$

The term η_g is taken as the expression for gas viscosity

$$\eta_g = 1/3 n m \bar{c} \lambda, \quad (14)$$

where n is the number of molecules per cc, m is the molecular mass, \bar{c} is the average and λ is the mean free path. Using kinetic theory considerations, this becomes

$$\eta_g = \frac{2}{3 \pi^{1/2} d^2} (mkT)^{1/2}, \quad (15)$$

where d is the molecular diameter. If we take $\lambda^2 \lambda_2 \lambda_3 / \lambda_1 = V_s / N$, and substitute equations (13) and (15) into equation (9), the result is:

$$\eta = \frac{Nh}{V} \frac{1}{(1 - e^{-\theta/T})} \frac{6}{n\kappa} \frac{V_s}{V - V_s} \exp \frac{a' E_s V_s}{(V - V_s) RT} + \frac{V - V_s}{V} \frac{(2mkT)^{1/2}}{3 \pi^{1/2} d^2} \quad (16)$$

If we apply equation (16) to argon, we get the results shown in Table 5. The calculated values, η (calc) I, II, and III were obtained from equation (16) by assuming the following three sets of values of a' and κ , respectively: $a' = 0$, $\kappa =$

TABLE 5
VISCOSITY OF ARGON IN MILLIPOISES

$T, ^\circ\text{K}$	V, cc	$\eta(\text{obs})^*$	$\eta(\text{calc})\text{I}^\dagger$	$\eta(\text{calc})\text{II}^\ddagger$	$\eta(\text{calc})\text{III}^\ddagger$
84.25	28.25†	2.82	2.82	2.82	2.82
86.25	28.59†	2.62	2.57	2.33	2.45
86.90	28.69†	2.56	2.51	2.22	2.35
87.30	28.73†	2.52	2.49	2.17	2.32
90.00	29.15	2.32	2.32	1.86	2.08
99.5	30.49	1.62	1.77	1.16	1.42
110.0	32.74	1.37	1.53	0.88	1.13
120	34.43	1.16	1.07	0.58	0.77
127	36.31	1.00	0.89	0.47	0.63
133.5	39.16	0.77	0.73	0.38	0.51
138.7	42.04	0.70	0.59	0.31	0.414
143	45.39	0.63	0.49	0.26	0.35
147	51.21	0.56	0.38	0.22	0.28
149	57.08	0.50	0.31	0.20	0.24

* Zhadanova, N. F., *Soviet Phys. J.E.T.P.*, 4, 749 (1957).

† Calculated from equation (16), see the text.

‡ These values were obtained by interpolating the data from the *International Critical Tables*, ed. E. W. Washburn (New York: McGraw-Hill, 1926). For other volume data, refer to Zhadanova, *op. cit.*

0.42; $a' = 0.01014$, $\kappa = 1$; and $a' = a = 0.00534$, $\kappa = 0.662$. One may see that the values of η (calc) I agree better than those of II and III. However, the value, $a' = 0$, is problematical, since the activation energy for flow, $a' E_s V_s / (V - V_s)$, should be equal or greater than the energy, $a E_s V_s / (V - V_s)$, which is necessary for a molecule occupying a neighboring vacancy (cf. Fig. 2). Thus, in the calculations of η (calc) III, a value of a' which equals a ($= 0.00534$) was assumed and κ ($= 0.662$) was determined so as to fit the viscosity at 84.25°K , whereas in the column of η (calc) II, κ was assumed to be unity and a' ($= 0.01014$) was determined. Both the η (calc) II and III decrease too rapidly. If one considers, however, that the temperatures in Table 5 range nearly from the melting to the critical temperatures and that the viscosities are at various vapor pressures from about 70,

to 48 atmospheres, it must be said that the agreement of η (calc) II and III with experiment is quite satisfactory. Our treatment of the viscosity of gas-like degrees of freedom as equal to the viscosity for a perfect gas can certainly be improved.

It is of interest to compare the above calculation of viscosity resulting in equation (16) with earlier procedures. Formerly the gas-like contribution to viscosity was neglected and the whole liquid treated as the relaxation of a lattice structure. This is a reasonable approximation near the melting point but becomes less appropriate with rise in temperature. The other improvement adopted here is the more explicit form that can now be written for the rate constant, k' , for the stress relaxation. The fact that in the current expression the fluidity is proportional to the number of holes $n(V - V_s)/V_s$ provides justification for a somewhat analogous relation found by Batschinski.⁸ It is especially satisfactory that our viscosity equation for the liquid passes over naturally into the gas equation. The present liquid theory also suggests that since $V - V_s$ becomes zero for the solid, the solid should become very viscous and further that nonequilibrium dislocations and vacancies must be chiefly responsible for the plasticity shown by solids. In earlier papers from this laboratory, a theory of the bulk viscosity of ordinary liquids⁹ and of polymers¹⁰ was developed. The authors used the earlier type of rate expression which did not explicitly include the factor, $(V - V_s)/V_s$, corresponding to the number of holes adjacent to a molecule. According to our present model of the liquid, the bulk viscosity should be the same as the shear viscosity except for a change in the meaning of the transmission coefficient, κ . For the bulk viscosity, κ , should express the chance that when a molecule jumps into a hole, the abandoned hole transforms into an elastically expanded lattice, a phonon, which then travels with the velocity of sound.

Any relaxation process involves a rate constant, $k' = \kappa(kT/h) (F^\ddagger/F_n) \exp(-\epsilon_0/kT)$, which has as one factor the ratio of the partition function for the activated state to the partition function for the normal state. If temperature or pressure brings a change in viscosity through modifying the partition function, F_n , for the normal state, the result is said to be due to a change in liquid structure. Such a structure change appears as a change also in the thermodynamic properties of the liquid. On the other hand, a similar change in viscosity may result from a change in the partition function, $F^\ddagger \exp(-\epsilon_0/kT)$, of the activated complex, and this is not reflected in the thermodynamic properties of the liquid. Thus, the development of the partition function of the liquid to explain thermodynamic properties is the necessary preliminary for deducing from viscosity the properties of the activated state. As a result of this study, we arrive at the picture of molecules of simple liquids shifting position chiefly by using vacancies and less frequently by making use of dislocations or fractional sized holes.

Diffusion.—A great deal of experimental evidence indicates that liquids subjected to stress relax by the same mechanism regardless of the nature of the stress. Thus, the activation energy for either ionic diffusion or conduction is ordinarily equal to the activation energy for viscous flow, indicating that the same elementary reactions are involved. Self-diffusion and viscous flow likewise show the same activation energy and therefore involve the same elementary process.

Consider the relationship between viscosity and diffusion. The diffusion coefficient is defined following Fick by the equation

$$J_i = -D_i \frac{dc_i}{dx} = u_i c_i. \quad (17)$$

Here J_i is the current density of matter of kind i . D_i , u_i , and c_i are the diffusion coefficient, velocity, and concentration of the i th kind of matter. In Figure 6, we have drawn a typical cross section of a condensed phase normal to the direction of flow. We suppose that molecule 7 diffuses upward by randomly jumping past the six articulating sectants 1 to 6. This is a necessary assumption, since the activation for shear mechanism is involved in diffusion. Now the rate of shear is

$$\dot{\gamma} = u/\lambda_1, \quad (18)$$

where u is the forward velocity of molecule 7 with respect to its neighbors. Further,

$$\eta_i = f_i/\dot{\gamma}, \quad (19)$$

where f_i , the shear stress, is the driving force on molecule 7 divided by the sum, A_i , of the six shear areas 1 to 6, that is, $A_i = 6 \lambda_2 \lambda_3$ or, for the most general packing, when instead of 6 there are ξ neighbors, $A_i = \xi \lambda_2 \lambda_3$ (see Fig. 6). Equations (18) and (19) are the relations which have been used in deriving (10).

Now for diffusion, the force on a molecule

$$\begin{aligned} F_i &= -\frac{d\mu_i}{dx} = -\frac{d}{dx} (kT \ln a_i + \mu_{0i}) \\ &= -kT \frac{d \ln a_i}{dx} = -kT \left(\frac{d \ln a_i}{d \ln c_i} \right) \frac{1}{c_i} \frac{dc_i}{dx}. \end{aligned} \quad (20)$$

Here μ_i , μ_{0i} , and a_i are the chemical potential, the chemical potential at unit concentration, and the activity a_i of the i th component. Also, we have

$$f_i = F_i/A_i = \frac{-kT}{\xi \lambda_2 \lambda_3} \left(\frac{d \ln a_i}{d \ln c_i} \right) \frac{1}{c_i} \frac{dc_i}{dx} \doteq \eta_i \dot{\gamma}. \quad (21)$$

Combining equations (18), (19), and (21) with (17) yields

$$D_i = \frac{\lambda_1 kT}{\xi \lambda_2 \lambda_3 \eta_i} \frac{d \ln a_i}{d \ln c_i} \simeq \frac{kT}{\xi (V/N)^{1/3} \eta_i} \frac{d \ln a_i}{d \ln c_i}. \quad (22)$$

Equation (22) may be used to calculate the diffusion coefficient of argon at 84.12°K, here $a_i = c_i$. We take $\xi = 6$, $V = 24.98$ cc, and Zhadanova's value¹¹ for the viscosity, $\eta = 2.82 \times 10^{-3}$ poises. This gives $D = 1.98 \times 10^{-5}$ cm² sec⁻¹ as compared with Corbett and Wang's observed value¹² $D = 2.07 \times 10^{-5}$ cm² sec⁻¹.

An alternative procedure in deriving equation (22) is to follow Einstein in equating the Stokes hydrodynamic viscous drag on a sphere,¹³

$$F_i = 6\pi r \eta u \frac{\beta r + 2\eta}{\beta r + 3\eta}, \quad (23)$$

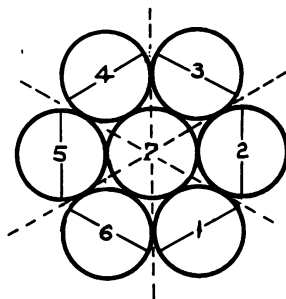


FIG. 6.—Hexagon normal to the direction of self-diffusion of molecule 7 in a close-packed liquid. Molecule 7 is diffusing forward.

to the thermodynamic drag, equation (20). The resulting equation is solved for u , which when introduced into equation (17) leads to

$$D = \frac{kT}{6\pi r\eta} \frac{d \ln a}{d \ln c} \left(\frac{\beta r + 2\eta}{\beta r + 3\eta} \right)^{-1}. \quad (24)$$

All the quantities except β , the coefficient of sliding friction, have been defined previously. β is the coefficient by which the relative velocity of two neighbors in contact must be multiplied to give force per unit area. If there is no slip at the interface, i.e. β is very large, the denominator in equation (24) is $6\pi r\eta$, while if $\beta = 0$, the denominator becomes $4\pi r\eta$. $4\pi r$ is the circumference of the circle drawn through the centers of the molecules 1 to 6, while $\xi(V/N)^{1/3}$, which plays the same role in equation (22), is the sum of the lengths of the straight lines which form the closed polygon joining the centers of the molecules 1 to 6. Equation (22) gives an excellent account not only of self-diffusion but also of mixed diffusion in uncomplicated cases.¹⁴ The significant structure method with its recourse to absolute rate theory for treating relaxation problems has obvious advantages over hydrodynamics because of the limited number of models having tractable hydrodynamic solutions. This is exemplified by the calculation of the viscosity of a high polymeric system for which it is necessary to treat the random walk of a group of connected segments.¹⁵ Onsager¹⁶ has written an interesting review of theories of diffusion.

The significant structure model also gives a very satisfactory account for liquids of the coefficients of expansion, of compressibility, and therefore of C_p .¹⁷ The thermal conductivity κ_l of liquids is represented rather well by an equation, $\kappa_l = \kappa_s V_s/V + \kappa_g(V - V_s)/V$, as shown by Walter Davis in a thesis in this laboratory. Here the subscripts l , s , and g on kappa indicate liquid, solid, and gas, respectively. That such a simplified model of the liquid state should represent thermodynamic and transport properties with the accuracy shown above is amazing. The significant structure method thus provides a new point of departure for treating all types of pure liquids and solutions.

Certain refinements of our theory are indicated:

1. Hole-hole interactions should be treated explicitly.
2. Dislocations, fractional-sized holes, stacking faults, and structures of the type discussed by Bernal¹⁸ are sufficiently abundant to eliminate long-range order.
3. The long-range order which Debye finds in the critical region should appear as a consequence of a complete liquid theory.
4. Where there is pronounced structure change upon melting, as in the case of water, the values of E_s , V_s , and θ must be appropriately modified.

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A MATHEMATICAL AID IN OPTIMIZING ENGINEERING DESIGNS

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Introduction and Results.—An engineer is frequently faced with the problem of optimizing a design to obtain a minimization of total operating costs. The writer has found that in an important class of such problems the desired minimum can be found directly without recourse to the laborious procedure of first solving for the optimum value of the parameters and then substituting back into the cost equation or to the soulless operation of a machine which gives numerical answers but no insight. The purpose of this note is to present this direct solution.

In the class of problems to which the present technique is applicable, the operation cost C is expressed as a polynomial of the independent parameter. The technique is restricted, however, to the case where the polynomial contains one more term than the number of independent parameters. Thus, if we denote our parameters by $x_1, x_2, \dots, x_\sigma$, we are to minimize the cost

$$C(x_1, x_2, \dots, x_\sigma) = \sum_{i=1}^n T_i$$

where
$$T_i = a_i \prod_{j=1}^{\sigma} x_j^{\beta_{ij}},$$

and where we have the restriction $n = \sigma + 1$.

The first step in our technique is to find a product of our n terms, each raised to an appropriate exponent α_i , which contains none of our σ parameters. This product we write as

$$\prod_{i=1}^n T_i^{\alpha_i} = K$$

Such a set of α 's is unique, apart from a common factor. In order to render the α 's completely unique, we impose a normalization condition

$$\sum_{i=1}^n \alpha_i = 1.$$